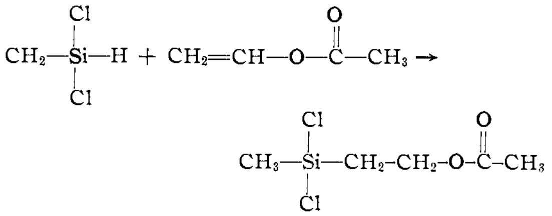
COMMUNICATIONS TO THE EDITOR

APPLICATION OF NUCLEAR MAGNETIC RESONANCE SPECTRA IN STRUCTURE DETERMINATION OF ISOMERIC SILICON HALIDES[1]

Sir:

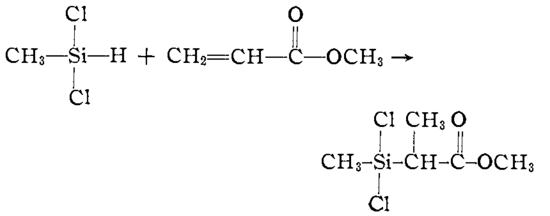
The well-known addition of the elements of the Si–H bond to a vinyl group (or, generally, to carbon–carbon unsaturation) has been shown to be catalyzed by peroxides and ultraviolet light and, in these cases, has been regarded as a typical free-radical reaction.[2] The reaction has also been carried out thermally and with the aid of platinum and palladium catalysts,[3] but there has been no speculation regarding the mechanism involved in these reactions. The addition has been shown to involve the addition of the silicon-containing group to the terminal carbon of the unsaturated reagent in several cases[4,5] and no example of a reversed addition orientation has been noted.

We have recently added methyldichlorosilane to a number of vinyl and allyl monomers using platinum-on-carbon as catalysts and Ionol as a polymerization inhibitor. Hydrolysis studies showed marked differences between the adducts from acrylonitrile and acrylate esters, on the one hand, and adducts from vinyl esters, vinyl ethers and the allyl monomers. The determination of structure of these adducts has been neatly resolved by the use of nuclear magnetic resonance spectra which shows that the reactions are



$$CH_2\text{—}\underset{Cl}{\overset{Cl}{Si}}\text{—}H + CH_2{=}CH\text{—}O\text{—}\overset{O}{\overset{\|}{C}}\text{—}CH_3 \rightarrow CH_3\text{—}\underset{Cl}{\overset{Cl}{Si}}\text{—}CH_2\text{-}CH_2\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3$$

(I)



$$CH_3\text{—}\underset{Cl}{\overset{Cl}{Si}}\text{—}H + CH_2{=}CH\text{—}\overset{O}{\overset{\|}{C}}\text{—}OCH_3 \rightarrow CH_3\text{-}\underset{Cl}{\overset{Cl}{Si}}\text{-}\overset{CH_3}{CH}\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_3$$

(II)

The NMR spectrum of (I) has two triplets formed by the spin–spin interactions of the two methylene groups. The spectrum of (II) has the doublet and quadruplet which result from the interactions of the protons in the $>CHCH_3$ group. The relative positions of the peaks due to the $-CH_2-O$ and CH_3-O groups in (I) and (II) respectively, are in the proper relationship to one another as determined with reference compounds. This is true, also, of the relative positions of the CH_3CO and $-CH-CO$ peaks in (I) and (II).

Compound (II) represents the first reported example of a reversed orientation in silane additions to vinyl groups.

The results of these experiments correlate well with an ionic mechanism in which the platinum catalyst promotes a $\overset{S^+}{CH_3SiCl_2}$ - - - $\overset{S^-}{H}$ polarization of the silane. Electrophilic attack of the silicon moiety initiates addition to vinyl acetate and nucleophilic attack of hydride ion initiates addition to methyl acrylate in a reaction which resembles the Michael addition.

Further details of these reactions will be submitted shortly.

We wish to acknowledge the aid of Robert C. Jones in obtaining these spectra.

Stanford Research Institute
Menlo Park, California
Varian Associates
Palo Alto, California

Leon Goodman
Robert M. Silverstein
James N. Shoolery

Received June 25, 1956

---

[1] This work was supported by Wright Air Development Command under Contract AF 33(616)-2998.

[2] L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, This Journal, **69**, 188 (1947).

[3] G. H. Wagner and C. O. Strother (to Union Carbide and Carbon), U. S. 2,632,013, March 17, 1953.

[4] G. H. Wagner, D. L. Bailey, A. N. Pines, M. L. Dunham and D. B. McIntire, *Ind. Eng. Chem.*, **45**, 367–74 (1953).

[5] J. W. Curry, This Journal, **78**, 1686 (1956).

HYDROLYSATES FROM SODIUM TRIMETAPHOSPHIMATE

Sir:

Contrary to the literature,[1] acid hydrolysis of trimetaphosphimate proceeds largely through intermediate ring compounds with one, two, and to some extent, three oxygens successively replacing the original imide linkages. Chain imidophosphates are never present in large amounts. While possible paths are outlined below, the main sequence of hydrolysis follows the solid arrows (see chart).

The first intermediate in this hydrolysis was isolated by Stokes[1] and prepared by a different method by de Ficquelmont,[2] both reporting it to be the chain diimidotriphosphate. However, repetition of either preparation yielded ring products, essentially DITMP with some ITMP.

The above sequence of reactions is dependent on formation of P–O–P linkages by elimination of NH_3 between P–OH and P–NH_2 groups (NH_3 detected by (1) consumption of acid and (2) odor upon rendering hydrolysate alkaline with NaOH). The yield depends on the extent of competition from the amide hydrolysis P–NH_2 + H_2O → P–OH + NH_3. The condensation reaction is quite general. For instance, ortho- and amidomonophosphate yield up to 15% pyrophosphate in acid solution (*p*H 3–4, 60°). Stokes[1] isolated 15% pyrophosphate from IDP hydrolysates (10 minutes boiling, dilute acetic acid). Chromatographic evidence for

---

[1] H. N. Stokes, *Am. Chem. J.*, **18**, 629–63 (1896).

[2] A. M. de Ficquelmont, *Ann. Chim.*, **12**, 169–280 (1939).